Review

Review of non-platinum anode catalysts for DMFC and PEMFC application

Alexey Serov [1,*], Chan Kwak

Corporate R&D Center, Samsung SDI, Shin-dong 575, Yeongtong-gu, Suwon-si, Gyeonggi-do, 443-731, South Korea

ABSTRACT

Articles devoted to non-platinum anode catalysts for DMFC and PEMFC application, operated in acidic media were reviewed. Several classes of possible platinum substitutes based on transition metal carbides, oxides, alloys and new exotic catalysts were described, with focus on synthetic methods, corrosion stability and activity in reactions of methanol/hydrogen oxidation. Directions for future research in field of non-platinum anode materials were discussed.

© 2009 Elsevier B.V. All rights reserved.

Contents

1. Introduction

Price of energy resources significantly increased in last years, followed by massive search for new alternative sources of energy. One of the promising fields of clean and sustainable power is fuel cell technology, based on direct conversation of fuel into electricity. Several hundreds of academics research articles and reports from commercials R&D centers are published every year to promote appearance of fuel cell into the market. At the present moment the main factor preventing fuel cells from successful commercialization is their high price. Making step from prototypes to mass production, it is possible to reduce manufacture expenses, but it will not affect on materials costs. Fuel cells operated at ambient conditions use platinum and platinum alloys for the conversation of fuel at the anode side, as well as for oxygen

reduction at cathode side. It is obvious, that high cost of platinum significantly increases total price of fuel cell devices. Solving this problem in short-term aspect can be reached by using less platinum at both anode and cathode sides [1,2], but for wide use of fuel cells, platinum alternatives (non-platinum catalysts) should be used [3–13].

Analysis of literature shows, that in last years tremendous progress in improvements of activity and stability of non-platinum cathode catalysts was achieved [14–17]. Materials used in fuel cells for oxygen reduction can be separated into three classes: heat treated macrocyclic compounds of transition metals [3–6], ruthenium based chalcogenides [7–13,17] and palladium alloys catalysts [14–16]. Among these classes, most promising catalysts are palladium alloys and high loaded RuSe/C [14–17]. Palladium and ruthenium are more preferable for general usage in fuel cell devices, due to lower price and higher mining capacity in comparison with platinum. Significant activity in research of oxygen reduction catalysts lead to feasibility of platinum substitution from cathode side.

Replacement of platinum and platinum alloys from anode side is not well investigated. There are several works devoted to using

* Corresponding author. Tel.: +41 56 5345251; fax: +41 56 3104435.
  E-mail addresses: alexey.serov@psi.ch (A. Serov), kcpmhkj@yahoo.com (C. Kwak).
[1] Present address: Paul Scherrer Institute, 5232 Villigen PSI, Switzerland.

non-platinum anode catalysts with alkaline electrolytes [18–20] for oxidation of liquid fuels, like methanol and ethanol. The anode reactions with alkaline membrane are much easier than those with acid membrane because oxygen ions from cathode help the fuel reduction in alkaline membrane fuel cell. The facilitative reaction mechanism of alkaline membrane fuel cell promotes the development of non-platinic anode catalysts. However, alkaline membranes for production of membrane electrode assembly (MEA) are still under investigation, and cannot compete with widely used and commercially available cation-exchange Nafion™ type membranes.

Different aspects of conventional platinum anode catalysts such as preparation methods, composition, support effect etc are well discussed and reviewed [21]. In contrast, limited publications describing non-platinum anode catalysts can be found and they are not well organized. At the present review we have summarized available data dedicated to using non-platinum anode catalysts in acidic media, analyzed feasibility of platinum substitution onto novel materials and suggested possible research directions for new non-Pt anode catalysts development.

2. Non-platinum catalysts based on transition metal carbides

Possibility of using transition metal carbides as catalysts for hydrogen oxidation was investigated from the end of sixties by Böhm and Pohl [22]. It was shown that tungsten carbide/carbon catalyst can be used in fuel cell operated both hydrogen and CO-rich "town gas" [22]. Later several groups investigated tungsten based materials for application as electrocatalysts in reaction of hydrogen oxidation [23–27]. These catalysts not only show significant activity towards hydrogen oxidation, but also high tolerance to presence of CO and H_2S. Last fact makes WC more preferable anode material for PEMFC in comparison with platinum, which is easily deactivated even by trace amounts of sulfur compounds or CO.

Recently several works dealing with using tungsten and molybdenum materials in PEMFC and DMFC applications were published [28–31]. Variable parameters affecting on catalytic activity in case of W and Mo carbides were: preparation method, carburization method and carburization temperature. For example, thin films of WC and W_2C can be prepared by magnetron sputtering with control of tungsten–carbon ration [29]. The authors shown by XRD measurement that prepared catalysts are single phased W_2C and WC. Surprising difference in stability both on air and during CV measurements in 0.5 M H_2SO_4 solution saturated by N_2 was determined (Fig. 1). It was found that WC film is stable at anode potentials below 0.6 V, demonstrating the potential use of WC as an anodic electrocatalyst in the DMFC. In contrast, W_2C does not have a stable region, causing immediate oxidation to form W_xO_y species when exposed to air or in an electrochemical environment. Considering reasonable stability of WC the authors performed investigation of CH_3OH adsorption. As it is shown in Fig. 2, adsorption of methanol results in the cleavage of the O–H bond with formation of methoxy intermediate (CH_3O) at 200 K. This is evident by absence of a $\upsilon(OH)$ feature at ~3240 cm^{-1}. In the same work films of WC were modified by low coverage by platinum and methanol adsorption shows a promoting effect of Pt for the dissociation of methoxy in the temperature range of 400–500 K. The surface science results suggest a synergistic effect for supporting low coverage of Pt on WC films for the potential application as electrocatalysts.

Several WC and WMC (where M = Co, Ni) were prepared by different chemical methods and tested in reaction of hydrogen oxidation in presence of CO [28]. Preparation was made in two steps, first was synthesis of precursors (co-precipitated W–Co alloy, peroxopolytungstic acid (PPTA) and $NiWO_4$) followed by nitrocarburization or isothermal carburization (applied to $NiWO_4$
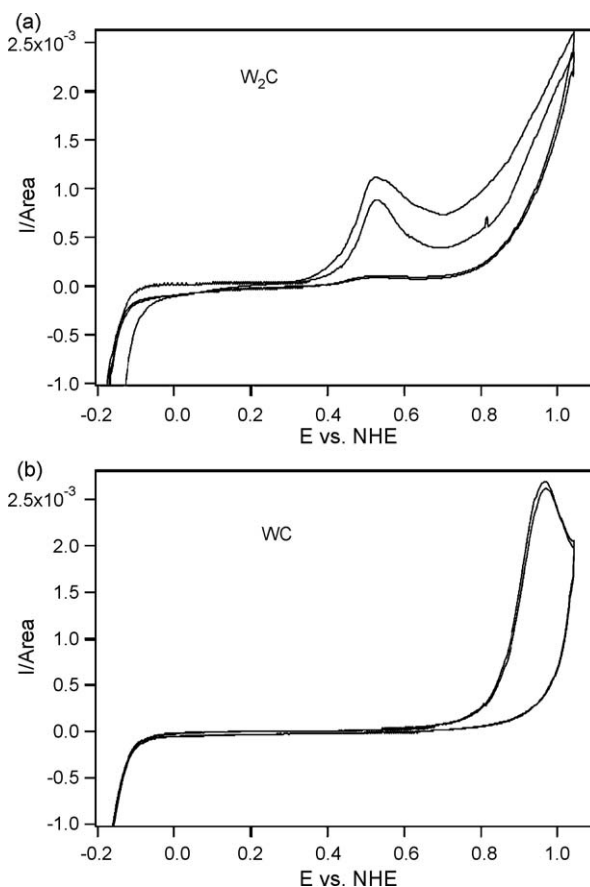
Fig. 1. Electrochemical CV measurements performed in 0.5 M H_2SO_4 saturated with N_2 of (a) W_2C and (b) WC films on carbon paper. For measurements, a 45 s conditioning period holding the working electrode at 0.05 and a linear ramping rate of 10 mV s^{-1} was used from −0.2 to −1.0 V and then back to −0.2 V. The CV curves were measured following two consecutive cycles. Voltages are normalized with respect to the normal hydrogen electrode [29].

precursor). For comparison, commercially available WC and nitrocarburized WO_3 were investigated. Electrodes for testing corrosion stability and activity in reaction of hydrogen oxidation were fabricated from prepared powder samples. Fig. 3 presents a typical graph of current density as a function of time, from a potentiostatic transient taken on WC made from nitrocarburized WO_3. It was found that with time the corrosion current falls to very low levels. It should be mentioned that hydrogen oxidation current rises as a function of time and continues to do so through the recording period. Fig. 3 also shows the typical effect from the presence of CO; a small reduction (~2.1%) in the magnitude of the H_2 oxidation current. Reversibility of the CO effect is illustrated in Fig. 4. The rising oxidation current on pure H_2 is interrupted and reduced by the introduction of 1% CO in the gas mixture. With CO in the gas, the current falls but by only about 3% and levels off instead of continuing to increase. When the CO is removed from the gas mixture, the H_2 oxidation current rises to its earlier levels and continues to increase with time, returning the electrode to its prior state. From present investigation the authors made next conclusions: WC shows a small and reversible reduction in the magnitude and rate of rise of the hydrogen oxidation current when 1% CO is added to a hydrogen fuel gas, on WC electrocatalysts, the reduction in H_2 oxidation rate due to the presence of CO is ~2–6%, the effect of CO on WC appears to be independent of electrode potential and independent of synthesis route, the effect of CO on WC appears to be the result of very weak surface adsorption which temporarily blocks the most active catalytic sites for H_2 oxidation.
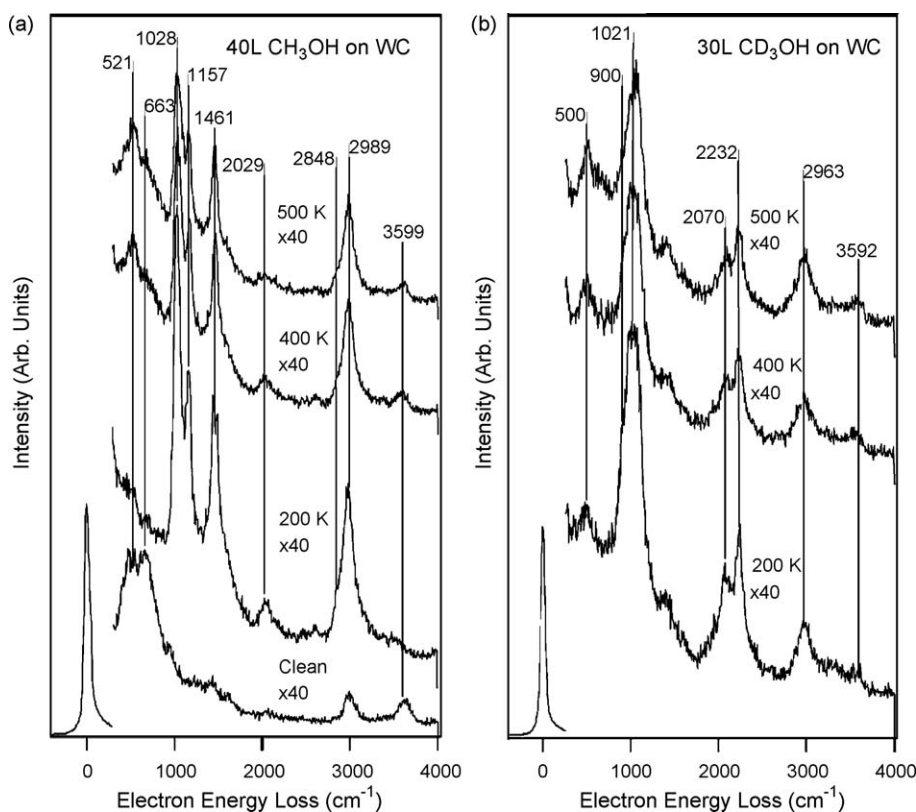
Fig. 2. HREEL spectra monitoring the thermal decomposition of (a) 40 L CH_3OH and b) 30 L CD_3OH on the WC film [29].

Attempt to investigate MoCo carbide catalyst as possible anode material in PEMFC was made by Izhar and Nagai [31]. As well as in case tungsten carbides, the authors used two-step procedure. First, oxidized alloy of MoCo were prepared with following carburization from 723–973 K at the rate of 1 K min^{-1} with 20% CH_4/H_2 (99.999%), and maintained at its final temperature for 2 h. Ketjen carbon (Cabot Co.) was then mixed with the Co–Mo carbides in methanol so that the concentration of the catalyst was 30 wt% followed by drying overnight in air. The membrane electrode assembly (MEA) was prepared in house by a common method [32]. Pre-treated membrane sheet (Nafion 117; Du Pont Co.) was covered from both sides by CoMoC/KC (anode) and 20 wt% Pt/C (cathode) and hot pressed

between two sheets of carbon cloths (Toray Co). The I–V curves of the KC supported Co–Mo carburized at 800, 823, 873, 923 and 973 K and Pt in the single-stack fuel cell at the anode are shown in Fig. 5. The open circuit voltages ranged between 0.90 and 0.92 V for the carbides and Pt catalyst. It was found that among the carburized catalysts, the CoMoC-873/KC displayed the highest performance. The cyclic voltammogram (CV) of the unsupported CoMoC-873 catalyst is presented in Fig. 6. The CV was measured from 0 to 1.1 V in 0.5 M sulfuric acid with a stream of flowing argon and hydrogen after
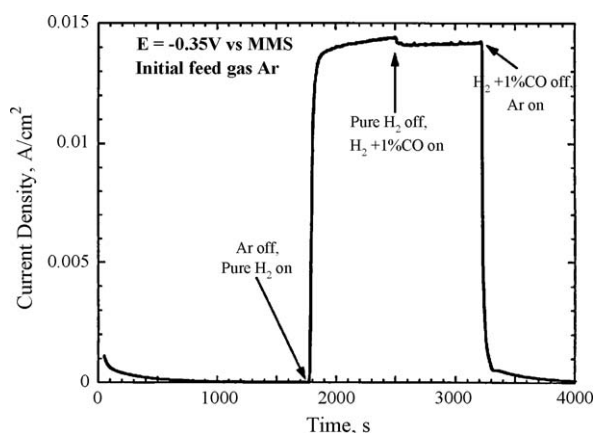

Fig. 3. Current as a function of time at −0.35 V vs. MMS on electrode II (WC made from nitrocarburized WO_3). The first 1750 s were under flow of Ar and show the passivating corrosion current. At 1750 s, pure H_2 was substituted for Ar. At 2500 s, pure H_2 was replaced by 1% CO/99% H_2 gas mixture. At 3200 s, the fuel supply was removed and replaced by Ar [28].
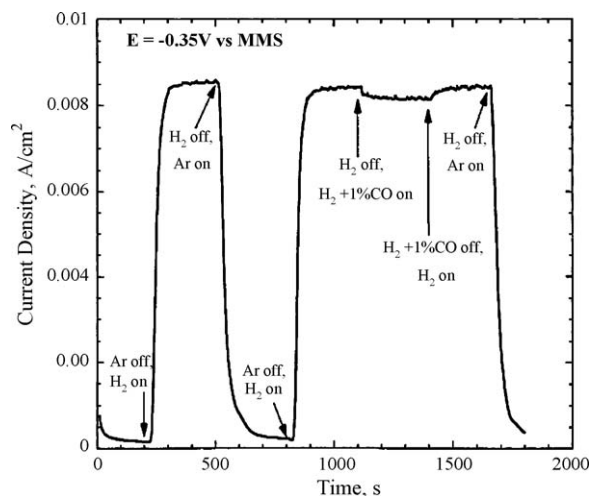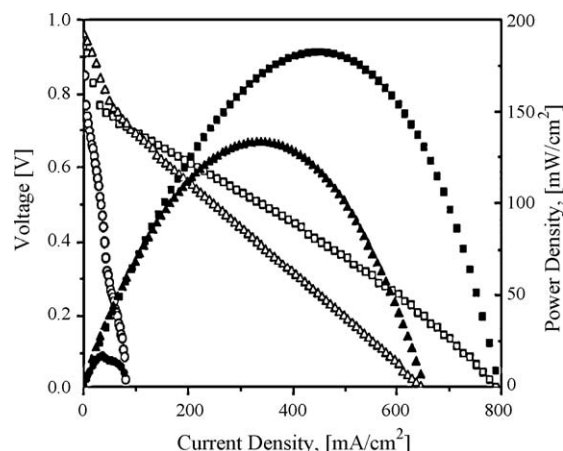

Fig. 4. Current as a function of time at −0.35 V vs. MMS on electrode III (WC made from nitrocarburized W–Co alloy). At 200 s, the initial flow of Ar was replaced by pure H_2. At 500 s, H_2 was replaced by Ar. At 800 s, H_2 was re-introduced into the fuel chamber. At 1100 s, pure H_2 was replaced by 1% CO/99% H_2 mixture. The 1% CO/99% H_2 mixture was removed after 1400 s and replaced with pure H_2. At 1650 s, H_2 was removed and Ar was re-introduced into the fuel chamber [28].
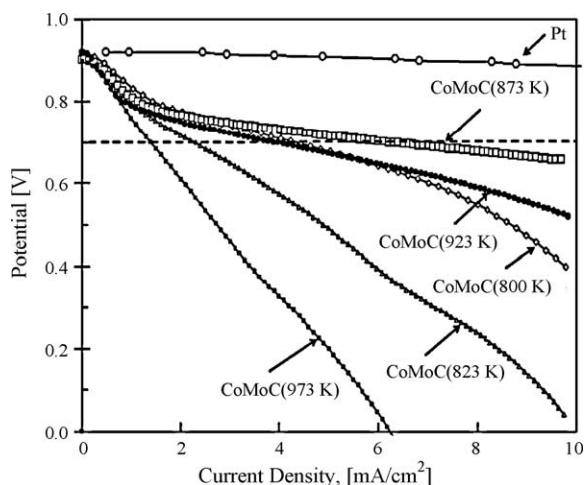
Fig. 5. The *I–V* curves of KC supported Co-Mo catalysts carburized at various temperatures and a 20 wt% Pt/C (not iR corrected). MEA: Nafion 117 (Du Pont Co.), catalyst loadings: anode (CoMoC), 1.0 mg cm^{-2}; cathode 1.0 (Pt) mg cm^{-2}. Cell operating conditions: cell temperature, 338K; reactant gasses, humidified at 353 K without back pressure, flow rate: 60 mL min^{-1} [31].

Fig. 7. *I–V* curves of the (□) commercial and (△) home-made 20 wt% Pt/C MEA, with (○) CoMoC-873, and power density curves of (■) commercial and (▲) in-house 20 wt% Pt/C MEA and (●) CoMoC-873 (not iR corrected), MEA: Nafion 117 (Du Pont Co.), catalyst loadings: anode (CoMoC), 1.0 mg cm^{-2}; cathode 1.0 (Pt) mg cm^{-2}. Cell operating conditions: cell temperature, 338 K; reactant gasses, humidified at 353 K without back pressure, flow rate: 60 mL min^{-1} [31].

reaching the steady state. The authors showed that at low potential, no peak corresponding to the redox reaction was observed. On the other hand, at a high potential (above 1 V), the catalyst exhibited a slight increase in current density probably due to corrosion. Fig. 7 shows the *I–V* characteristics for the single-stack fuel cell prepared using the commercial and home-made MEAs of the 20 wt% Pt/C catalyst. Almost identical performances were obtained for both systems near 0.65 V, but at a higher current density, the home-made MEA performance rapidly dropped. The current density at the maximum power output, I@PMax, obtained from CoMoC-873 was 37 mA cm^{-2}, and was 10.9% vs. the in-house Pt/C catalyst MEA (339 mA cm^{-2}). The BET area of the carbide samples are 0.4–49 m^2 g^{-1}, which is smaller than the usual platinum catalysts. The low performance of the carbide catalysts may originate from two factors: low surface area and the intrinsic activity of the carbide materials. Although the carbide electrodes had a performance significantly lower, than in Pt/C case, obtained results exhibits a positive step in the development of low cost Pt-free catalysts.

Recently, the same group of researchers investigated new electrocatalysts for PEMFC application [33,34]. Preparation and

characterization of catalysts was similar as published at [31]. The maximum power density for the 30% NiWC/KC carburized at 873 K was 8.2 mW cm^{-2} with a current density of 19.0 mA cm^{-2} and was 7.3% when compared to the 20 wt% Pt/C (111.7 mW cm^{-2}). The authors concluded that carburization temperature significantly affect on final electrocatalytic activity. It was found that tungsten carbides carburized at higher temperature were less active than catalysts treated at lower temperature. Such an effect can be explained by decreasing of active surface area of catalysts. During the evaluation of CoWC/KC and MoWC/KC the authors found that the maximum power densities of the 873 K-carburized CoWC/KB and MoWC/KB were 15.7 and 12.0 mW cm^{-2}, respectively, which were 14 and 11%, compared to a 20 wt% Pt/C catalyst [34]. After investigation of active sites of prepared catalysts it was found that they can be consisted of two types of material: metal carbides and metal oxycarbides. It was suggested by authors that CoW-oxycarbide and CoW-carbide species showed an intermediate number of active site, which results in the lower bond strength with hydrogen, thus promoting the charge transfer process. Thus, CoWC/KB with oxycarbide was more active for HOR while MoWC/KB without oxycarbide was less active [34].

It should be mentioned, that transition metal carbides were investigated no only as pure, non-platinum catalysts, but as possible support for platinum. Several groups studied electro-catalytic activity of different materials based on Pt-WC/C composites [35–48]. Chen and co-workers investigated catalytic activity of WC electrocatalysts as well as Pt mono- and submonolayers deposited on WC [35–38]. It was found that platinum and tungsten carbide produce synergetic system with catalytic activity significantly higher that in case of WC or Pt (at the same amounts). The same result was observed and published by group of Lee and co-workers [39–41]. Despite of such a composites can not be considered as fully platinum free, it should be noticed that results from mentioned above researches show, that amount of platinum in such a catalysts can be reduced dramatically while performance is compatible or even higher in comparison with commercial Pt-based catalysts.

3. Non-platinum catalysts based on promoted transition metal oxides

Catalysts based on transition metal oxides modified by platinum group metals attract attention of researchers due to
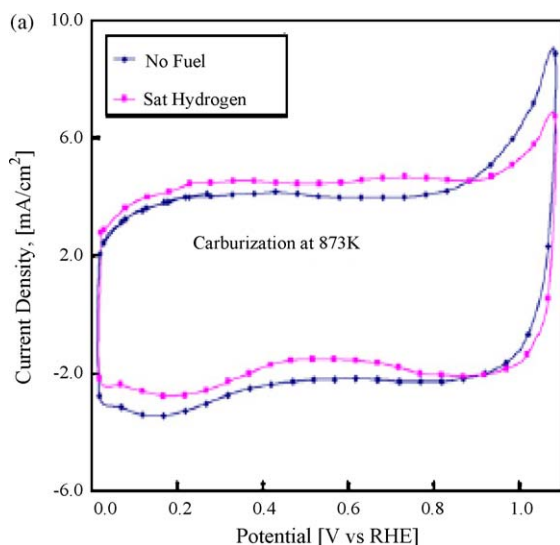
Fig. 6. Voltammetric measurements of CoMoC-873 in a stream of argon and hydrogen [31].
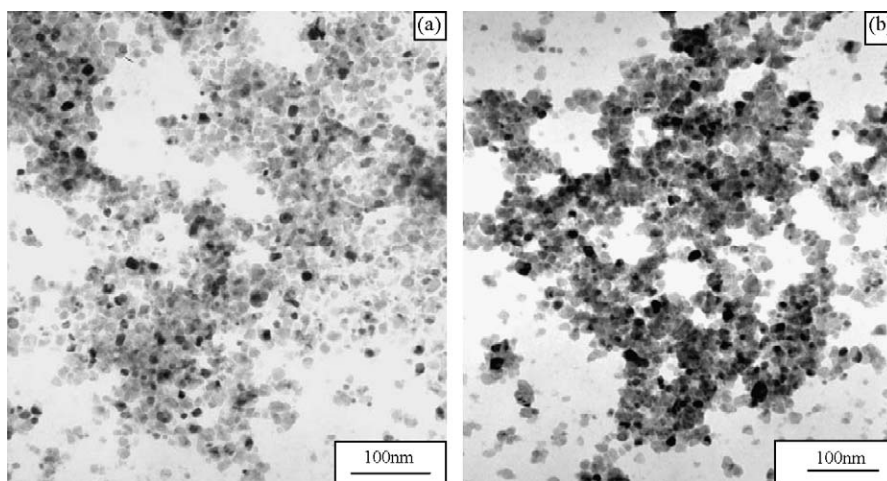
Fig. 8. TEM images of TiO$_2$ hydrolyzed from TiCl$_4$ (a) and Ti(OBu)$_4$ (b) [50].

their possible application as anode material in DMFC applications. It was shown that, for example, TiO$_2$ has high activity in oxidation of small organic molecules [48]. During the modification of TiO$_2$ electrodes by platinum, synergetic effect was noticed that revealed enhanced catalytic activity in the oxidation of adsorbed CO [49]. It should be mentioned that oxide material should be stable in acidic conditions, which exist at DMFC operation. At [48] was shown that TiO$_2$ is stable not only in acidic but also in alkaline media, and can be used as material for anodic electrooxidation of methanol.

Recently Liu et al. investigated catalytic activity of TiO$_2$ nanotubes modified by deposition of palladium nanoparticles [49]. The authors studied dependence of methanol oxidation activity from morphology of modified TiO$_2$ (nanoparticles or nanotubes) and from content of deposited palladium, pure palladium nanoparticles as well as TiO$_2$ nanoparticles were investigated. Synthesis of TiO$_2$ nanoparticles was performed by sol–gel method, previously described in [51], while TiO$_2$ nanotubes were synthesized by hydrothermal method [50]. Conventional reduction method with glycol was selected for palladium nanoparticles deposition on prepared TiO$_2$ material. TEM images of different TiO$_2$ were shown in Figs. 8 and 9. It is clearly seen that particle size in case of TiO$_2$ nanoparticles is about 10 nm, particles are well distributed with some regions of agglomerations. Nanotubes have outer diameter about 15 nm and inner diameter about 10 nm with longitude as long as few hundred nanometers. Electrochemical activity of prepared catalysts was investigated using three-electrode cell. Fig. 10 shows CV data for methanol

oxidation by pure TiO$_2$, modified TiO$_2$ and non-supported palladium nanoparticles. Result of CV analysis shows that most active catalyst is TiO$_2$ nanotubes modified by Pd, because TiO$_2$ nanotubes have a small size in diameter and therefore higher specific surface area inside and outside, which is preferable for the electrocatalyst. During the investigation of Pd loading effect, the authors found that catalysts with 3 wt% possess the highest activity in reaction of methanol oxidation in acid media. They suggested possible explanation of this experimental fact by agglomeration of palladium on the surface of titania with increasing of Pd loading. It can be concluded that Pd-TiO$_2$(nanotubes) catalysts after certain improvement can be used in new generation of fuel cells operated with platinum catalysts.

Modified manganese oxides are second class of possible anode materials for DMFC application. Constructed from [MnO$_6$] octahedral they can form different types, characterized by presence of channel structures. Manganese oxides historically were used as oxidation catalysts, ion-exchange materials, sensors etc [52,53]. At present moment they are intensively used in dry cells and primary batteries. Several works can be found about using MnO$_2$ as catalyst for fuel cells operated in alkaline media [54,55].

Effect of modification manganese oxide by iron, nickel and ruthenium was investigated by Fernandes and co-workers [56,57]. Fe–MnO$_x$ and Ni–MnO$_x$ were prepared by thermal decomposition of corresponding nitrates on platinum foil. Electrooxidation of methanol was investigated in dependence of calcination temperature and different Ni:Mn composition. Comparison of catalytic
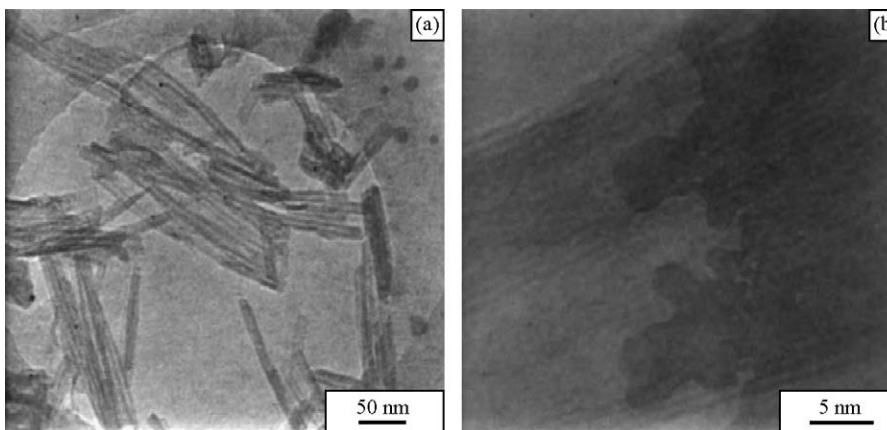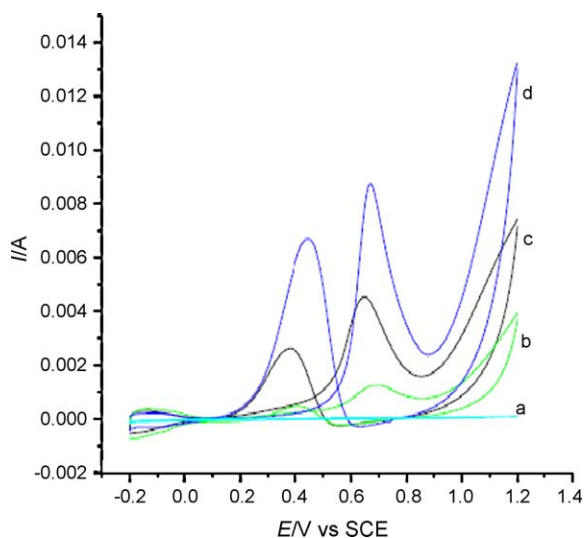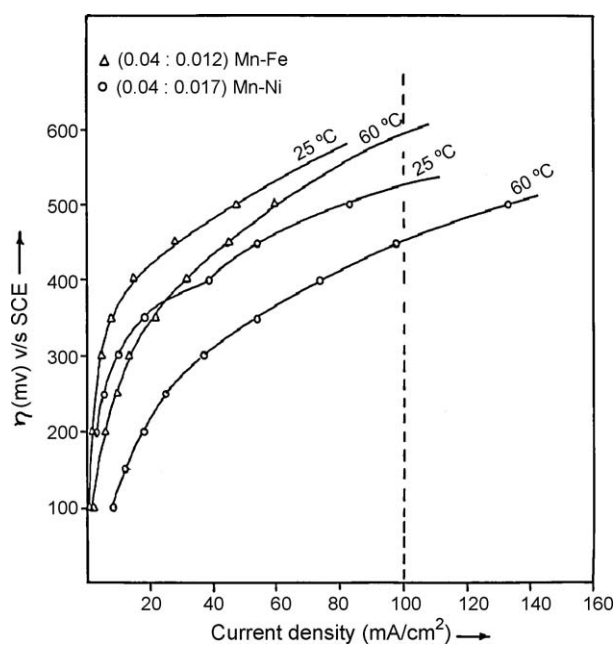

Fig. 9. High-resolution TEM images of TiO$_2$ nanotubes [50].
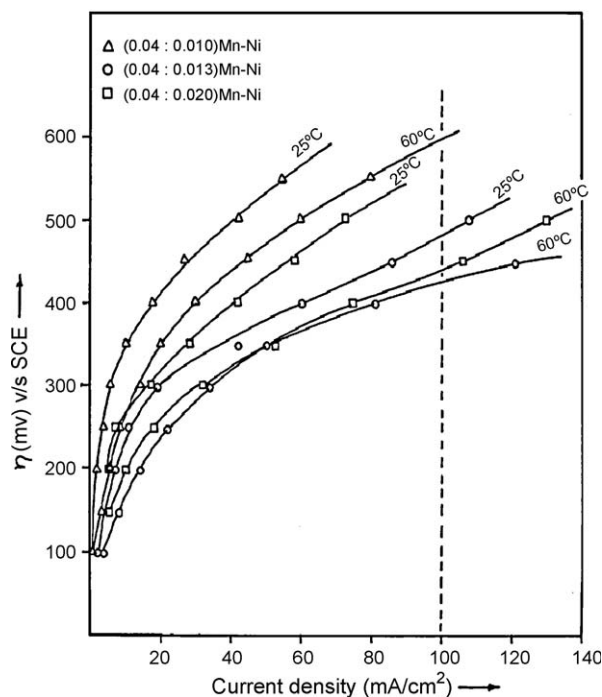
Fig. 10. Cyclic voltammograms in 1 M CH_3OH + 1 M H_2SO_4 for a Pd catalyzed reduction of $PdCl_2$ by glycol ethanol) TiO_2 nanotube dispersed with Nafion solution on Ti: (a) pure TiO_2 nanotubes; (b) non-supported Pd: (c) 3 wt% Pd–TiO_2 nanoparticles; (d) 3 wt% Pd–TiO_2 nanotubes. Scan rate 50 mV s^{-1} [50].

activity for Fe–MnO_x and Ni–MnO_x is shown in Fig. 11. It can be seen that nickel modified MnO_x possesses superior catalytic activity in contrast with iron based manganese oxide. Influence of Ni:Mn ratio on catalytic activity is shown in Fig. 12. Strong dependence of methanol oxidation activity from concentration of Ni was shown. The authors investigated the effect of calcination temperature on catalytic activity and found that most active catalysts can be synthesized at T = 450 °C (Fig. 13). Based on experimental results it can be concluded that heat treatment temperature, concentration and nature of dopant are main factors affecting on catalytic activity.

The same group later investigated possible use of carbon supported manganese octahedral molecular sieves (OMS-2) and mixture of commercially available Ru/C with OMS-2 for methanol
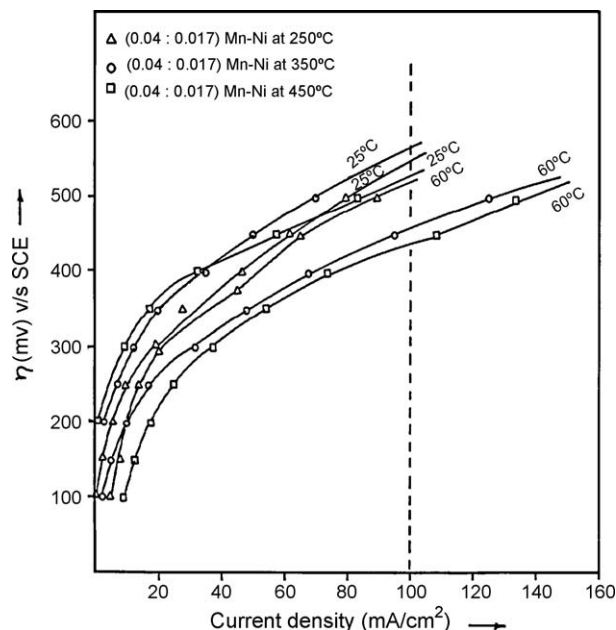

Fig. 12. Polarization curves (2.5 M H_2SO_4, 1 M CH_3OH) for electrooxidation of methanol on modified manganese dioxide electrodes at 25 and 60 °C as a function of molar composition of Ni^{2+} [56].

electrooxidation [57]. MnO_x in form of OMS-2 (marked by authors as S) was synthesized by oxidation of manganese sulfate with $KMnO_4$ [58]. For comparison of activity, a pyrolusite manganese oxide (marked by authors as P) was synthesized by the thermal decomposition of $Mn(NO_3)_2$ at 200 °C. It was shown by chemical analysis that OMS-2 samples has composition $MnO_{1.86}$ corresponding to average oxidation state of manganese of 3.72. From the other side, the pyrolusite sample prepared by thermal decomposition of Mn(II) nitrate has a stoichiometric composition of MnO_2 wherein the oxidation state of manganese is 4+. Prepared

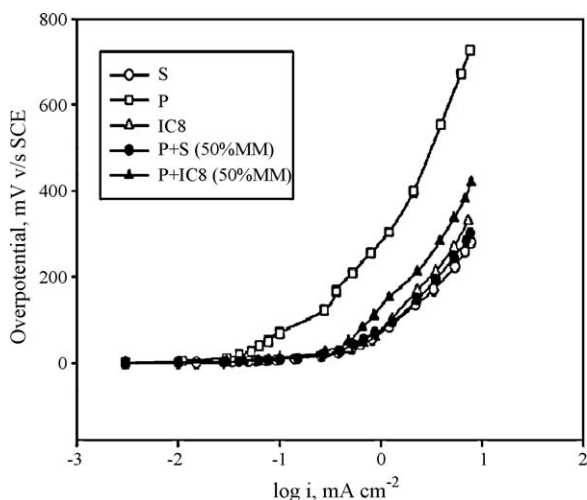**Fig. 11.** Polarization curves (2.5 M H_2SO_4, 1 M CH_3OH).for electrooxidation of methanol on modified manganese dioxide electrodes at 25 and 60 °C [56].

Fig. 13. Polarization curves (2.5 M H_2SO_4, 1 M CH_3OH) for electrooxidation of methanol on modified manganese dioxide electrodes at 25 and 60 °C as a function of the temperature of heat treatment (250, 350 and 450 °C) [56].

Fig. 14. Tafel plots to study effect of pyrolusite (P) on OMS-2 (S) and nsutite (IC8) [57].

catalysts were electrochemically characterized in 2.5 mol L^{-1} H$_2$SO$_4$ and 1 mol L^{-1} CH$_3$OH solution, using three-electrode scheme. Analysis of catalytic activity reveals the fact that OMS-2 sample possesses higher activity in comparison with other manganese oxides (Figs. 14 and 15). The authors explained this fact by the presence in OMS-2 structure of active Mn^{4+}/Mn^{3+} redox couple. The synergetic effect of combination Ru/C with OSM-2 was detected and can be explained in terms that Ru acts as nucleating centers for CO clustering within the octahedral sieve framework of OMS-2 and promotes, facile oxidation of CO to CO$_2$.

4. Other non-platinum anode catalysts for DMFC application

Metal alloys of noble metals (Pt, Pd, Ru, Os etc) with base metals (Fe, Co, Ni etc) are well investigated in reaction of oxygen reduction [59–63]. Some platinum based alloys, especially PtRu are widely studied in direct alcohol fuel cells [64]. In contrast only few works about using non-platinum alloys for methanol electrooxidation can be found.

Mayanna and co-workers investigated catalytic activity of electrodeposited PdNi alloy [65]. Samples with different morphology can be prepared by controlling current density, pH and temperature of solution. PdNi films with different palladium content were synthesized and their activity for the reaction of
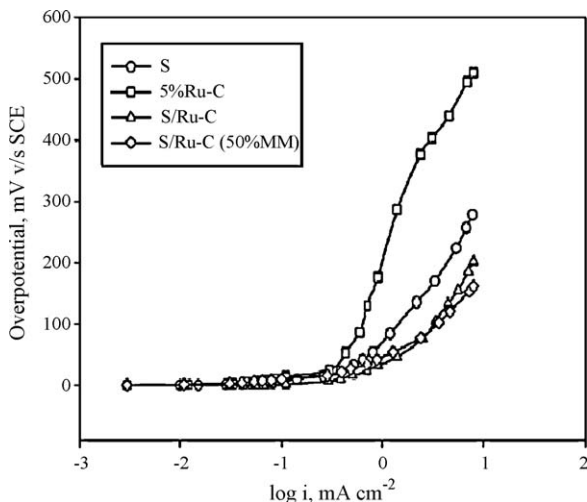
Fig. 15. Tafel plots of OMS-2 (S), 5%Ru–C and their mixtures [57].
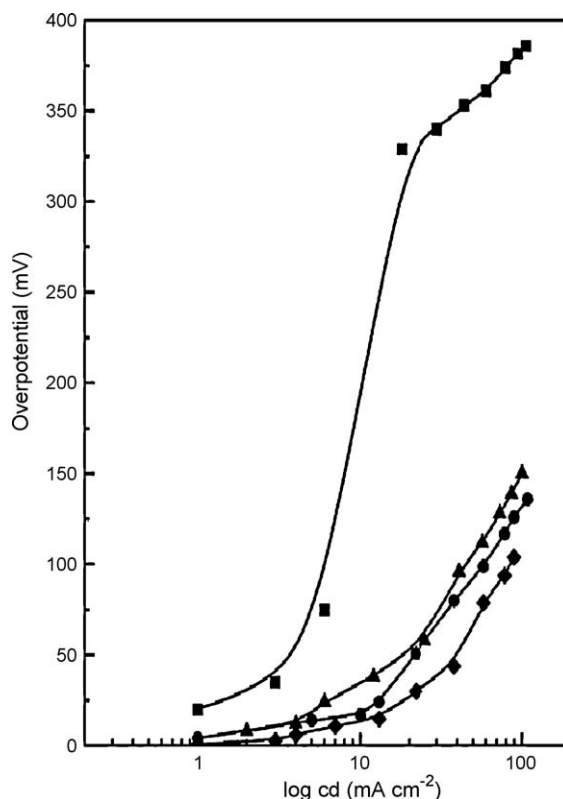
Fig. 16. Polarization curves for methanol oxidation on Ni–Pd alloy films of different compositions in 1 M CH$_3$OH + 0.5 M H$_2$SO$_4$ at 323 K, ($\bullet$) 64% Pd, ($\blacktriangle$) 33% Pd, ($\blacksquare$) 20% Pd, and ($\blacklozenge$) 6% Pd [65].

methanol oxidation was studied (Fig. 16). A catalyst with the highest palladium concentration possesses the highest activity, which can be explained by decreasing crystallites size with increasing of Pd loading.

During evaluation of osmium based alloys (OsSn, OsMo, OsV) in reaction of methanol and sodium borohydride Northwood and co-workers showed that such alloys are totally inactive to methanol electrooxidation [66]. Such experimental observation contradicts therefore, the theoretical suggestion by Kua and Goddard [67], based on the bi-functional mechanistic model, indicating electro-catalytic activity for Os toward methanol oxidation.

New exotic electrocatalyst based on dispersed gold nanoparticles onto a polyaniline (PANI) grafted multiwall carbon nanotube (MWNT-g-PANI) matrix was prepared through a two-step electro-chemical process [68]. The authors show that Au nanoparticles dispersed into PANI-grafted MWNT exhibit the essential characteristics, including enhanced electrocatalytic activities for methanol oxidation, restricted poisoning influence from adsorbed carbon monoxide, better oxidation kinetics, and performance at elevated temperatures, for use in DMFC applications. It was observed that the composite electrode consisting of MWNT, PANI, and Au^0 nanoparticles exhibit superior electrocatalytic activity compared with catalysts comprising MWNT and Au^0 nanoparticles and pristine Au electrode. Preparation method suggested in the above mentioned work is simple and provides future opportunities to use other conducting polymers and metal/alloy nanoparticles in generating other advanced catalysts for fuel cell applications and other devices.

Metal-free carbon nitride nanotubes were synthesized by template method and were used as catalysts for methanol electrooxidation [69]. Due to weak catalytic activity of prepared catalysts (Fig. 17) at the present stage of research it is not feasible to use them as alternative to platinum catalysts. However, after further investigations of catalytic mechanisms and optimization of
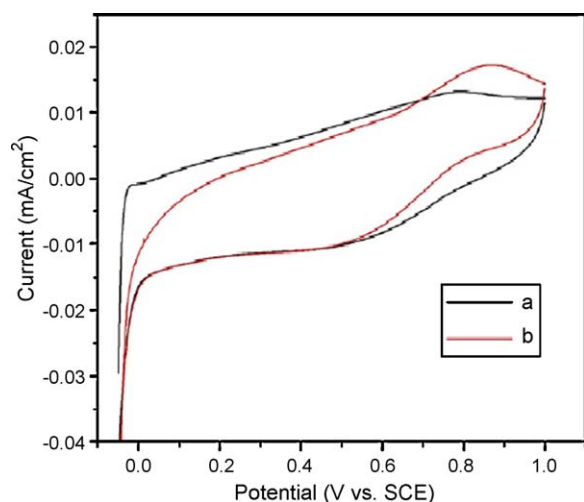
Fig. 17. Cyclic voltammograms of (a) CNNTs in 0.5 mol dm^{-3} H$_2$SO$_4$ aqueous solutions, (b) CNNTs in 0.5 mol L^{-1} H$_2$SO$_4$ aqueous solutions containing 1 mol L^{-1} CH3OH, at scan rate 10 mV s^{-1} and room temperature [69].

electrocatalytic properties the authors proposed to use them as support material for more active anode materials.

5. Conclusions

In the present review we summarized available information about possible use of Pt-free anodes for DMFC and PEMFC application. The acidic atmosphere by the ionomer restricted the candidates of non-platinic materials. The stability for the redox potential and fuel atmosphere also affected on the material choice. Among the tried materials, transition metal carbides and promoted oxides can be successfully used for methanol and hydrogen oxidation.

There are two kinds of advantages of non-platinic catalysts, i.e. low prices and strong resistance to poisonous substances. Hydrocarbon fuels are foreseen to be used for fuel cells around twenty years from now until large amount of hydrogen is available from renewable energies. The resistance for CO and methanol will be a key factor of anode catalyst materials as far as methanol is used for small fuel cells and reformate gas is used for power generation fuel cells.

As it followed from present review the performance of non-platinic catalysts is much lower than that of the platinum, therefore very limited comparison of MEA performance has been reported. Based on our knowledge such a difference in activity can be affected by several parameters, for example, surface area, particle size, intrinsic properties of non-platinum catalysts etc. From our point of view additional investigations pointed to promotion effect of base metal in case of oxide and alloyed catalysts are needed. New catalysts based on metal free carbon nitride nanotubes are promising material for using as support for either conventional or new electrocatalysts.

References

[1] S. Ye, A. Vijh, L. Dao, J. Electroanal. Chem. 415 (1996) 115–121.
[2] J. Fournier, G. Faubert, J.Y. Tilquin, R. Cote, D. Guay, J.P. Dodelet, J. Electrochem. Soc. 144 (1997) 145–154.
[3] M. Lefevre, J.P. Dodelet, P. Bertrand, J. Phys. Chem. B 106 (2002) 8705–8713.
[4] S. Baranton, C. Coutanceau, C. Roux, F. Hahn, J.-M. Leger, J. Electroanal. Chem. 577 (2005) 223–234.
[5] A.J. Wagner, G.M. Wolfe, D.H. Fairbrother, Appl. Surf. Sci. 219 (2003) 317–328.
[6] P.H. Matter, L. Zhang, U.S. Ozkan, J. Catal. 239 (2006) 83–96.
[7] N. Alonso-Vante, W. Jaegermann, H. Tributsch, W. Honle, K. Yvon, J. Am. Chem. Soc. 109 (1987) 3251–3257.
[8] A.K. Shukla, R.K. Raman, Annu. Rev. Mater. Res. 33 (2003) 155–168.
[9] N. Alonso-Vante, H. Tributsch, O. Solorza-Feria, Electrochim. Acta 40 (1995) 567–576.
[10] M. Bron, P. Bogdanoff, S. Fiechter, I. Dorbandt, M. Hilgendorff, H. Schulenburg, H. Tributsch, J. Electroanal. Chem. 500 (2001) 510–517.
[11] N. Alonso-Vante, M. Fieber-Erdmann, H. Rossner, E. Holub Krappe, Ch. Giorgetti, A. Tadjeddine, E. Dartyge, A. Fontaine, R. Frahm, J. Phys. IV Fr. 7 (1997) 887–890, C2.
[12] V.I. Zaikovskii, K.S. Nagabhushana, V.V. Kriventsov, K.N. Loponov, S.V. Cherepanova, R.I. Kvon, H. Bönnemann, D.I. Kochubey, E.R. Savinova, J. Phys. Chem. B 110 (2006) 6881–6890.
[13] M. Hilgendorff, K. Diesner, H. Schulenburg, P. Bogdanoff, M. Bron, S. Fiechter, J. New Mater. Electrochem. Syst. 5 (2002) 71–81.
[14] W.E. Mustain, K. Kepler, J. Prakash, Electrochem. Commun. 8 (2006) 406–410.
[15] W.E. Mustain, J. Prakash, J. Power Sources 170 (2007) 28–37.
[16] A.A. Serov, S.-Y. Cho, S. Han, M. Min, G. Chai, K.H. Nam, C. Kwak, Electrochem. Commun. 9 (2007) 2041–2044.
[17] A.A. Serov, M. Min, G. Chai, S. Han, S. Kang, C. Kwak, J. Power Sources 175 (2008) 175–182.
[18] H. Heli, M. Jafarian, M.G. Mahjani, F. Gobal, Electrochim. Acta 49 (2004) 4999–5006.
[19] K.A. Assiongbon, D. Roy, Surf. Sci. 594 (2005) 99–119.
[20] F.P. Hu, P.K. Shen, J. Power Sources 173 (2007) 877–881.
[21] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D.P. Wilkinson, J. Power Sources 155 (2006) 95–110.
[22] H. Böhm, F.A. Pohl, Wiss. Ber., AEG-Telefunken 41 (1968) 46.
[23] K. von Benda, H. Binder, A. Köhling, G. Sandstede, From Electrocatalysis to Fuel Cells, University of Washington Press, Seattle, 1972, pp. 87–100.
[24] P.N. Ross, P. Stonehart, J. Catal. 39 (1975) 298.
[25] P.N. Ross, P. Stonehart, J. Catal. 48 (1977) 42.
[26] J.B. Christian, R.G. Mendenhall, US Patent 6,656,870, 2003.
[27] J.B. Christian, R.G. Mendenhall, US Patent 7,060,648, 2006.
[28] D.R. McIntyre, G.T. Burstein, A. Vossen, J. Power Sources 107 (2002) 67–73.
[29] M.B. Zellner, J.G. Chen, Catal. Today 99 (2005) 299–307.
[30] J.B. Christian, S.P.E. Smith, M.St. Whittingham, H.D. Abruña, Electrochem. Commun. 9 (2007) 2128–2132.
[31] S. Izhar, M. Nagai, J. Power Sources 182 (2008) 52–60.
[32] Th. Frey, M. Linardi, Electrochim. Acta 50 (2004) 99–105.
[33] M. Nagai, M. Yoshida, H. Tominaga, Electrochim. Acta 52 (2007) 5430–5436.
[34] S. Izhar, M. Yoshida, M. Nagai, Electrochim. Acta 54 (2009) 1255–1262.
[35] E.C. Weigert, A.L. Stottlemyer, M.B. Zellner, J.G. Chen, J. Phys. Chem. C 111 (2007) 14617–14620.
[36] H.H. Hwu, K. Kourtakis, J.G. Lavin, J.G. Chen, J. Phys. Chem. B 105 (2001) 10037–10044.
[37] M.B. Zellnera, J.G. Chen, J. Electrochem. Soc. 152 (2005) A1483–A1494.
[38] N. Liu, K. Kourtakis, J.C. Figueroa, J.G. Chen, J. Catal. 215 (2003) 254–263.
[39] R. Ganesan, J.S. Lee, Angew. Chem. Int. Ed. 44 (2005) 6557–6560.
[40] D.J. Ham, Y.K. Kim, S.H. Han, J.S. Lee, Catal. Today 132 (2008) 117–122.
[41] R. Ganesan, D.J. Ham, J.S. Lee, Electrochem. Commun. 9 (2007) 2576–2579.
[42] Y. Hara, N. Minami, H. Itagaki, Appl. Catal. A: Gen. 323 (2007) 86–93.
[43] G. Lu, J.S. Cooper, P.J. McGinn, J. Power Sources 161 (2006) 106–114.
[44] H. Meng, P.K. Shen, Z. Wei, S.P. Jiang, Electrochem. Solid State Lett. 9 (2006) A368–A372.
[45] H. Zheng, Z. Gu, J. Zhong, W. Wang, J. Mater. Sci. Technol. 23 (2007) 591–594.
[46] M.K. Jeona, K.R. Lee, W.S. Lee, H. Daimon, A. Nakahara, S.I. Woo, J. Power Sources 185 (2008) 927–931.
[47] C.A. Angelucci, L.J. Deiner, F.C. Nart, J Solid State Electrochem. 12 (2008) 1599–1603.
[48] D.B. Chu, X.F. Zhou, C.J. Lin, Chem. J. Chinese U 21 (2000) 133.
[49] J.H. Liu, C.B. Yu, Chem. J. Chinese U 24 (2003) 2263.
[50] M. Wang, D.-J. Guo, H.-L. Li, J. Solid State Chem. 178 (2005) 1996–2000.
[51] S.Y. Chae, M.K. Park, S.K. Lee, T.Y. Kim, S.K. Kim, W.I. Lee, Chem. Mater. 15 (2003) 326.
[52] J.S. Rebello, J.B. Fernandes, Ind. J. Chem. A 43A (2004) 1676–1679.
[53] S.L. Suib, Chem. Innovations 30 (2000) 27.
[54] D. Zhang, D. Chi, T. Okajima, T. Ohsaka, Electrochim. Acta 52 (2007) 5400–5406.
[55] F.H.B. Lima, M.L. Calegaro, E.A. Ticianelli, Electrochim. Acta 52 (2007) 3732–3738.
[56] P.V. Samant, J.B. Fernandes, J. Power Sources 79 (1999) 114–118.
[57] J.S. Rebello, P.V. Samant, J.L. Figueiredo, J.B. Fernandes, J. Power Sources 153 (2006) 36–40.
[58] R.N. DeGuzman, Y.F. Shen, E.J. Neth, S.L. Suib, C.L. O'Young, S. Levine, J.M. Newsam, Chem. Mater. 6 (1994) 815.
[59] O. Savadogo, K. Lee, K. Oishi, S. Mitsushima, N. Kamiya, K.-I. Ota, Electrochem. Commun. 6 (2004) 105–109.
[60] W. Wang, D. Zheng, C. Du, Z. Zou, X. Zhang, B. Xia, H. Yang, D.L. Akins, J. Power Sources 167 (2007) 243–249.
[61] F.H.B. Lima, M.J. Giz, E.A. Ticianelli, J. Braz. Chem. Soc. 16 (2005) 328.
[62] J. Batista, A. Pintar, J.P. Gomilšek, A. Kodre, F. Bornette, Appl. Catal. A: Gen. 217 (2001) 55–68.
[63] W.E. Mustain, K. Kepler, J. Prakash, Electrochim. Acta 52 (2007) 2102.
[64] S. Wasmus, A. Kuver, J Electroanal Chem. 461 (1999) 14–31.
[65] T. Shobha, C.L. Aravinda, P. Bera, L.G. Devi, S.M. Mayanna, Mater. Chem. Phys. 80 (2003) 656–661.
[66] M.H. Atwan, D.O. Northwood, Elod L. Gyenge, Intl. J. Hydrogen Energy 30 (2005) 1323–1331.
[67] J. Kua, W.A. Goddard III, J. Am. Chem. Soc. 121 (1999) 41.
[68] P. Santhosh, A. Gopalan, K.-P. Lee, J. Catal. 238 (2006) 177–185.
[69] X. Lu, H. Wang, S. Zhang, D. Cui, Q. Wang, Solid State Sciences 11 (2009) 428–432.